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PREPARATION AND PROPERTIES OF THE ESTERS OF TETRAMETHYLETHYLENEGLYCOLPHOSPHOROUS ACID

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I. INTRODUCTION

Study of the activity of phosphorus trichloride on glycols began with the works of P. Carre. (1)

In later years A. Ye. Arbuzov, V. M. Zoroastrovnya, N. I. Rizpolozhenskiy, P. A. Rossiyskaya, and M. I. Kabachnik (2 - 4) have shown that PCl_3 reacts with glycols to form the acid chlorides of glycolphosphorous acids, and that N. A. Menshutkin's acid chlorides react with glycols to form compound cyclic esters of glycolphosphoric acids.

Cyclic esters of phosphorous acids have a series of interesting properties which are to a considerable degree dependent on the structure of the glycol. Previous experiments were conducted with double-primary or primary-secondary glycols.

This article describes the derivation of several esters from tertiary glycols. Investigations were conducted on the activity of PCl_3 and the Menshutkin acid chlorides on double-tertiary alpha-glycol-tetramethylethyleneglycol.

As a result of the action of PCl_3 on tetramethylethyleneglycol the cyclic acid chloride or tetramethylethyleneglycolphosphoric acid was derived (the reaction occurring in the presence of pyridine):

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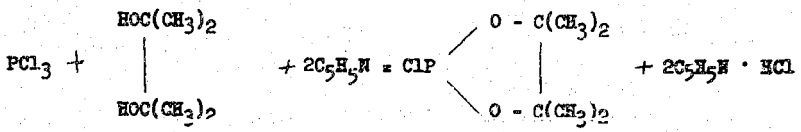
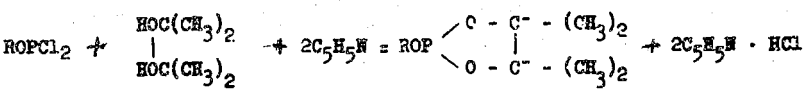
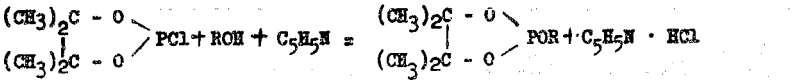


Two methods ware used in the synthesis of the cyclic esters of tetramethylethyleneglycolphosphorous acid:

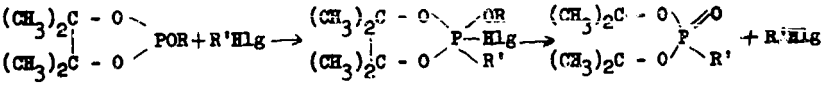
1. Action of the Menshutkin acid chlorides on tetramethyleneglycol (in the presence of pyridine):



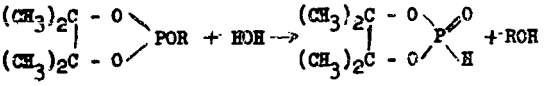
2. The interaction of the acid chloride of tetramethylethyleneglycolphosphorous acid and alcohol (in the presence of pyridine):



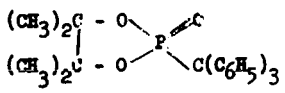
The methyl, ethyl, n-propyl, and n-butyl esters of tetramethylethyleneglycolphosphorous acid were synthesized. These acid chlorides and esters are very reactive compounds. The interaction of the esters of tetramethylethyleneglycolphosphorous acid with halides and water was studied. In all cases the reaction proceeded without cleavage of the ring. Splitting of a halogen bond occurred according to the schemes below, when the esters were reacted with halides.



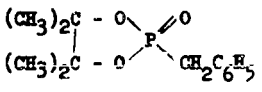
When the esters were acted on by water, there was a formation of alcohol:



As a result of the reactions of the esters with the halides triphenylbromomethane, benzyl chloride, and benzoyl chloride, the crystalline tetramethylethyleneglycol esters of triphenylmethylphosphonic acid or the other corresponding phosphonic acids could be isolated as the final products.



Benzylphosphonic acid



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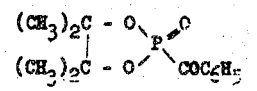
Benzoylphosphonic acid

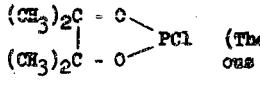


The products of the reactions of the esters with ethyl bromide and ethyl iodide -- acetyl tetrachloride and acetyl chloride (liquids with high boiling points) -- are not obtained in their pure form because they decompose upon distillation in a vacuum (1-2 millimeters of mercury).

During the interactivity of the acid chloride and the esters of tetramethylethyleneglycolphosphorous acid with water, tetramethylethyleneglycolphosphorous acid is prepared.

II. RESULTS OF EXPERIMENTS

A. Action of Phosphorus Trichloride on Tetramethylethyleneglycol



(The acid chloride of tetramethylethyleneglycolphosphorous acid)

The experiment was carried out in a round-bottomed flask equipped with a reflux condenser and a stirrer which contained 11.8 grams of pinacol, 15.8 grams of pyridine, and 80 milliliters of dry ester. 13.8 grams of PCl_3 were slowly added from dropping funnel. The flask was cooled with ice water. Pyridine hydrochloride began to precipitate immediately. After the ingredients had been added, the flask was heated for 30 minutes in a hot-water bath. After cooling, the residue was separated, washed with dry ether, and after the ether was removed, the residue was distilled in vacuum.

First Distillation:

First fraction, 50-88 degrees at 17 mm of mercury - 1.5 g
Second fraction, 88-91 degrees at 17 mm of mercury - 9 g

The residue in the flask (about one half of the original volume of the liquid) decomposes under formation of red phosphorus. After cooling in the distillation flask, the pinacolphosphoric acid crystals precipitated.

The fraction with boiling point 88-91 degrees at 17 millimeters of mercury, in the second distillation, gave:

First fraction, 80-81.5 degrees at 13 mm of mercury - 3 g
Second fraction, 81.5-82 degrees at 13 mm of mercury - 5.6 g
} 47 % of the theoretical

The fraction with boiling point 81.5-82 degrees at 13 millimeters of mercury is the pure acid chloride of tetramethylethyleneglycolphosphorous acid. This acid chloride, a colorless, easily flowing liquid which fumes powerfully in the air, gives a strong exothermic reaction with water, and changes into crystalline tetramethylethyleneglycolphosphorous acid.

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Properties:

d_0^{20} 1.1562; d_{20}^{20} 1.1586; n_D^{20} 1.4720

Found: MR_D 44.08

Calculated: MR_D 44.05

0.1448 g substance: 45.01 ml NaOH (T = 0.01934) (Neyman's analysis used for phosphorus determination)

0.1241 g substance: 39.14 ml NaOH

1 ml NaOH (T = 0.01934) combines with 0.5353 mg phosphorus

Found %: P 16.63; 16.88

Calculated %: P 16.98 $C_6H_{12}O_2PCl$

0.0992 g substance: 0.0770 g AgCl (chlorine determined by precipitation from acid chloride aqueous solution with a 5-percent solution of $AgNO_3$ with quantitative (gravimetric) determination of AgCl)

0.0954 g substance: 0.0735 g AgCl

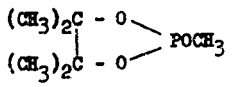
Found %: Cl 19.19; 19.06

Calculated %: Cl 19.44 $C_6H_{12}O_2PCl$

The fraction 80-81.5° at 13 mm is a less pure form of the acid chloride.

B. Action of Menshutkin's Acid Chlorides on Tetramethylethyleneglycol

1. Methyl Ester of Tetramethylethyleneglycolphosphorous Acid



In this preparation, 16.5 grams of methoxydichlorophosphine were added to 14.6 pinacol and 19.5 grams pyridine dissolved in 100 milliliters of dry ether. The mixture was stirred and cooled. After the reaction, the pyridine hydrochloride was filtered off, the ether driven off, and the residue distilled in vacuum.

First Distillation:

First fraction 87-94 degrees at 56 mm of mercury
Second fraction 94-100 degrees at 56 mm of mercury - 14.5 g

A residue of 3 grams of pinacolphosphorous acid solidified in the form of white crystals on cooling.

The second fraction, in a repeated distillation, gave:

First fraction 78-91 degrees at 48 mm of mercury
Second fraction 91-92.5 degrees at 48 mm of mercury -- 17.3 g, (51.4% of the theoretical)

The fraction with boiling point 91-92.5 degrees at 48 millimeters of mercury, methyl ester of tetramethylethyleneglycolphosphorous acid, is a colorless,

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easily flowing liquid with an odor like that of trimethylphosphite. When exposed to air it quickly changes into crystalline pinacolphosphorous acid. Its reaction with water is strongly exothermic.

Properties

d_0^0 1.0522; d_0^{20} 1.0449; d_{20}^{20} 1.0469; n_D^{20} 1.4417

Found: MR_D 44.96

Calculated: MR_D 44.45

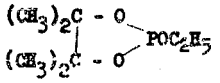
0.0778 g substance: 24.52 ml NaOH (T = 0.01998)

1 ml NaOH (T = 0.01998) combines with 0.5530 mg phosphorus

Found %: O 17.42

Calculated: P 17.41 $C_7H_{15}O_3P$

2. Ethyl Ester of Tetramethylethyleneglycolphosphorous Acid



This ester was obtained by the action of ethyl alcohol on the acid chloride of tetramethylethyleneglycolphosphorous acid.

In this preparation, 2.9 grams of ethyl alcohol were added to 11.5 grams of acid chloride and 4.9 grams of pyridine in a solution of dry ether. (While cooling the flask with ice water). The flask was heated for 20 minutes in a hot-water bath, and after cooling, the pyridine hydrochloride was filtered out. The ether was driven off, and the residue fractionated. Double distillation yielded the following fractions:

First fraction 72-74.5 degrees at 14 mm of mercury
Second fraction 74.5-75 degrees at 14 mm of mercury -

1.6 g, $n_D^{19.9}$ 1.4397

Third fraction 75-76 degrees at 14 mm of mercury -

4 g, n_D^{20} 1.4392

} 46.7 % of the theoretical

There was a residue of 1.5 grams of pinacolphosphorous acid.

The fraction with boiling point 75-76 degrees at 14 millimeters of mercury, ethyl ester of tetramethylethyleneglycolphosphorous acid, had properties similar to those of the previously described methyl ester, and its odor was similar to that of triethylphosphite.

Properties

d_0^0 1.0322; d_0^{20} 1.0156; d_{20}^{20} 1.0156; n_D^{20} 1.4392

Found: MR_D 49.74

Calculated: MR_D 50.06

0.1334 g substance: 39.74 ml NaOH (T = 0.01998)

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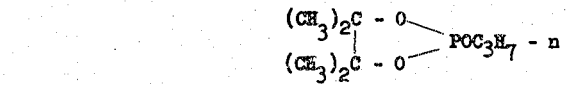
Properties (Contd)

Found %: P 16.47

Calculated %: P 16.14 $C_8H_{17}O_3P$

The fraction with boiling point 74.5-75 degrees at 14 millimeters of mercury is the less pure form of the ethyl ester of pinacolphosphorous acid.

3. n-Propyl Ester of Tetramethylethyleneglycolphosphorous Acid



Prepared similarly to methyl ester using 14.6 grams of pinacol, 19.6 grams of pyridine, and 20 grams of n-propoxydichlorophosphine dissolved in dry ether. Fractional distillation of the product of the reaction gave:

First fraction 84-86 degrees at 12 mm of mercury
Second fraction 86 degrees at 12 mm of mercury - 2 g - cloudy
Third fraction 86-89 degrees at 12 mm of mercury - 17.3 g
Residue - 2.6 g

After double distillation of the fraction with boiling point 86-89 degrees at 12 millimeters of mercury, 11.5 grams of substance with boiling point 84.5-86 degrees at 11.5 millimeters of mercury were obtained. This was 44.9 percent of the theoretical yield. n-propyl ester of tetramethylethyleneglycolphosphorous acid is a colorless liquid with a characteristic odor similar to aliphatic phosphites.

Properties

d_0^0 1.0138; d_0^{20} 0.9961; d_{20}^{20} 019981; n_D^{20} 1.4406

Found: MR_D 54.45

Calculated: MR_D 54.68

0.0492 g substance: 13.63 ml NaOH (T = 0.01998)

0.0959 g substance: 25.56 ml NaOH

Found %: P 15.11; 15.31

Calculated %: P 15.04. $C_9H_{19}O_3P$

4. n-Butyl Ester of Tetramethylethyleneglycolphosphorous Acid

This compound is prepared in the same way as the preceding compound, using 27.7 grams of pinacol, 41 grams of n-butoxydichlorophosphine, and 37.2 grams of pyridine dissolved in dry ether. Products of the reaction are distilled in a vacuum.

First distillation:

First fraction 55-103 degrees at 14.5 mm of mercury
Second fraction 103-110 degrees at 14.5 mm of mercury - 42 g
Third fraction 110-119 degrees at 14.5 mm of mercury - 1 g
The residue in the flask is pinacolphosphorous acid.

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In further separation, 34.32 grams of a fraction with a boiling point of 105-106.5 degrees at 14.5 millimeters of mercury were obtained from the fraction with a boiling point of 103-110 degrees at 14.5 millimeters of mercury after a second distillation. This yield is 66.5 percent of the theoretical.

Properties

d_0^0 1.0076; d_0^{20} 0.9901; d_{25}^{25} 0.9780; n_D^{25} 1.4413

Found: MR_D 59.39

Calculated: MR_D 59.29

0.0498 g substance: 13.48 ml NaOH (T = 0.01934)

0.1020 g substance: 27.08 ml NaOH

1 ml NaOH (T = 0.01934) unites with 0.5353 mg phosphorus

Found %: P 14.48; 14.21

Calculated %: P 14.09. $C_{10}H_{21}O_3P$

C. Interaction of the n-Butyl Ester of Tetramethylethyleneglycolphosphorous Acid and Water

To 4.4 grams of n-butyl ester was added 0.36 grams of water, slightly acidified with HCl. The temperature of the mixture went up to 80 degrees centigrade. Upon cooling, white crystals precipitated. The crystals were filtered off, and the filtrate, which had the odor of butyl alcohol, was distilled at 110-115 degrees.

The crystals, after double recrystallization from petroleum ether, acquired a constant melting point of 106.5-108 degrees. Tetramethylethyleneglycolphosphorous acid (white tetrahedral prisms) is very hygroscopic, quickly deliquesces in the air, and is very soluble in dioxane, less soluble in boiling petroleum ether, and is not soluble in ether or benzene.

The molecular weight (determined by the cryoscopic method in dioxane) was 161.7. The molecular weight of $C_6H_{13}O_3P$ is 164.

Properties

0.0626 g substance: 22.19 ml NaOH (T = 0.01934)

0.1470 g substance: 49.46 ml NaOH (T = 0.01998)

Found %: P 18.97; 18.60

Calculated %: P 18.90. $C_6H_{13}O_3P$

D. Interaction of Esters of Tetramethylethyleneglycolphosphorous Acid With Halides. Interaction of the n-Butyl Ester With Triphenylbromomethane

To one gram of the n-butyl ester was added a benzene solution of 1.45 grams of triphenylbromomethane. The mixture was heated to boiling for 5 minutes, and then the benzene was driven off in a hot-water bath. The residue crystallized, and the crystals were pressed out in a Nutsch filter. The filtrate (several drops) gives a reaction for halogen (according to Beilstein's test). In view of the small quantity, it was impossible to distill. The crystals after double recrystallization from benzene and then from ligroin had the melting point 231-231.5

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degrees. This substance is readily soluble in boiling benzene, less soluble in boiling ligroin, and is not soluble in ether. The reaction for halogen (according to the Beilstein test) is negative.

Properties

0.1049 g substance:	13.77 ml NaOH (T = 0.01998)
Found %:	P 7.25
Calculated %:	P 7.63. $C_{25}H_{25}O_3P$

By saponification with HCl, triphenylmethylphosphonic acid is prepared.

E. Interaction of the Methyl Ester With Triphenylbromomethane

Under the conditions of the preceding experiment, 0.5 gram of the methyl ester was acted on by 0.9 gram triphenylbromomethane. The formation of methyl bromide was observed during the reaction; this compound burns with a green-bordered flame. The product of the reaction, recrystallized from benzene, from ligroin, and again from benzene, had a melting point of 229.5-231.5 degrees. A mixed melting test with the substance prepared from the n-butyl ester did not show any depression.

F. Interaction of the n-Butyl Ester With Benzyl Chloride

In this preparation, 5.2 grams of butyl ester and 3 grams of benzyl chloride were heated in a sealed tube for 4 hours at 160 degrees. Then the product of the reaction was poured into a small Arbuzov flask. At a temperature of 120 degrees (on a hot bath), several drops of substance with boiling point of 74-75 degrees (butyl chloride -- Beilstein's test) were driven off. To avoid decomposition of the substance, the butyl chloride was drawn off in a vacuum; 1.9 grams of butyl chloride, or 90 percent of the theoretical yield, were obtained. The residue in the flask crystallized. On recrystallization from dry ether, the crystals had a boiling point of 115-116.3 degrees. The substance forms white needle-shaped crystals, readily soluble in benzene, petroleum ether, but less so in boiling ether.

Properties

0.0782 g substance:	17.77 ml NaOH (T = 0.01998)
0.0696 g substance:	15.64 ml NaOH
Found %:	P 12.41; 12.40
Calculated %:	P 12.20. $C_{13}H_{19}O_3P$

G. Interaction of the Esters With Benzoyl Chloride

1. In this preparation, 1.5 grams of benzoyl chloride were added to 2.3 grams of the n-propyl ester. An exothermic reaction was observed when these compounds were mixed.

The mixture was heated for 4 hours in a small flask equipped with a reflux condenser (the temperature of the hot water bath was 90-110 degrees). Then, propyl chloride was distilled off from the reacted mixture (boiling point 47-48 degrees). In several hours the residue crystallized. After two recrystallizations from ligroin the substance had a melting point of 90-91 degrees and formed white prisms and hydroscopic crystals (soluble in benzene, boiling ether, and ligroin).

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Properties

0.1224 g substance: 2652 ml NaOH (T = 0.01998)

Found %: P 11.98

Calculated %: P 11.56. $C_{13}H_{17}O_4P$

2. 1.6 grams of benzoyl chloride were added to 2 grams of the methyl ester. An exothermic reaction was observed during the mixing of these compounds, and methyl chloride was formed. Following the exothermic reaction, the mixture was heated for 30 minutes (the temperature of the hot water bath was 60-80 degrees); upon cooling, crystals formed. The weight of the crystals was 2.9 grams. Recrystallization from ligroin resulted in a substance melting at 89-90 degrees.

3. In similar fashion (to the two experiments described previously) one gram of the ethyl ester reacted with 0.7 gram benzoyl chloride. Formation of ethyl chloride was observed. The product of the reaction was the same as that derived with the n-propyl and the methyl esters. The tetramethylethyleneglycol ester of benzoylphosphonic acid with 1,4-dinitrophenylhydrazine forms a hydrazone with a boiling point of 194.5-195.5 degrees - yellow needles (from methyl alcohol).

H. Interaction of the n-Butyl Ester With Ethyl Bromide

Fifteen grams of the n-butyl ester and 7.4 grams of ethyl bromide were heated in a sealed tube at 160 degrees for 4 hours. The liquid separated into two layers, and from distillation of the upper layer were obtained 8.5 grams of a fraction with a boiling point of 97-110 degrees, or 91.4 percent of the theoretical yield of butyl bromide. The lower layer, composed of a liquid whose consistency resembled glycerine, decomposed during distillation in vacuum.

I. Interaction of n-Butyl Ester With Ethyl Iodide

In this synthesis, 4.3 grams of the n-butyl ester and 3 grams of ethyl iodide were heated in a sealed tube at 150-160 degrees for 3 hours. The liquid separated into two layers, the upper one yielding 2.5 grams of fraction with a boiling point of 122-127 degrees, or 71 percent of the theoretical yield of butyl iodide. The lower layer decomposed during distillation in a vacuum of one millimeter of mercury.

III. CONCLUSIONS

1. The action of phosphorus trichloride and Menshutkin's acid chlorides on tetramethylethyleneglycol was studied. The cyclic acid chloride of tetramethylethyleneglycolphosphorous acid was prepared.

The cyclic methyl, ethyl, n-propyl, and n-butyl esters of tetramethylethyleneglycolphosphorous acid were prepared.

2. The acid chloride and esters of tetramethylethyleneglycolphosphorous acid reacted with water to form cyclic tetramethylethyleneglycolphosphorous acid. The reactions proceeded without cleavage of the ring.

3. The esters of tetramethylethyleneglycolphosphorous acid reacted with halides without cleavage of the ring. As a result of the reaction the cyclic esters of phosphoric acid were converted into compounds with pentavalent phosphorus -- tetramethylethyleneglycol esters of the corresponding phosphonic acids.

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